Synthesis of 4-Alkoxynaphthyl Methyl Sulfide from 1-Alkoxy-4-thiocyanatonaphthalene and Methanol in the Presence of Cyanide Anion

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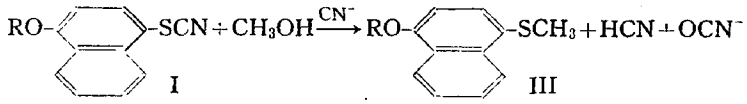
Synopsis

A facile methylation of 1-alkoxy-4-thiocyanatonaphthalene afforded 4-alkoxynaphthyl methyl sulfide (R; CH_3, C_2H_5, C_3H_7, C_4H_9, n-C_6H_{13}, n-C_8H_{17}, and n-$C_{12}H_{25}$). The formation of bis(4-alkoxynaphthyl) disulfide (R; CH_3 and C_2H_5) was found in several cases of this reaction. Four 4-alkoxynaphthyl methyl N-tosylsulfilimines (R; CH_3, C_2H_5, C_3H_7, and C_4H_9) were derived from these aryl methyl sulfides.

Introduction

Many sulfides including phenyl methyl sulfides are commercially available for pesticides. However, alkoxynaphthyl methyl sulfides have never been reported. Recently, Tanaka *et al.* reported[1] the formation of phenyl alkyl sulfide from phenyl thiocyanate and alcohol in the presence of cyanide anion. This method was successfully applied to synthesize 4-alkoxynaphthyl methyl sulfide (III) from 1-alkoxy-4-thiocyanatonaphthalene (I) and methanol in the presence of cyanide anion as follows:



(1)

I III

a R=CH_3 d R=C_4H_9 g R=n-$C_{12}H_{25}$

b R=C_2H_5 e R=n-C_6H_{13}

c R=C_3H_7 f R=n-C_8H_{17}

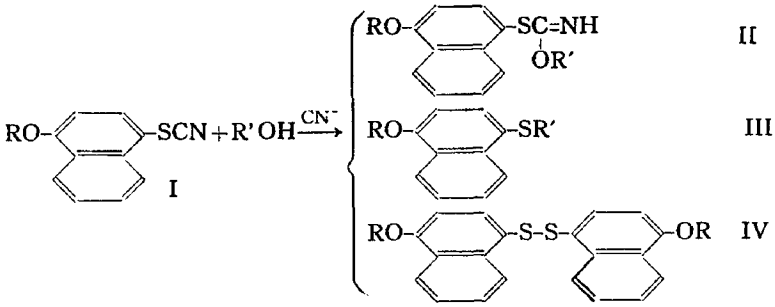
The synthesis of I was already reported in our previous paper.[2]

During the course of an investigation of the reaction conditions for the synthesis of III we found the formation of bis(4-alkoxynaphthyl) disulfide (IV) in several cases. This paper is conecrned with the synthesis of 4-alkoxynaphthyl methyl sulfide and the formation of bis(4-alkoxynaphthyl) disulfide as well as the synthesis of 4-alkoxynaphthyl methyl N-tosylsulfilimine (V) derived from these new naphthyl methyl sulfides.

Results and Discussion

Syntheses of Sulfides and Sulfilimines. The reaction of I with methanol in the presence of an equimolecular amount of NaCN proceeded readily in general by heating

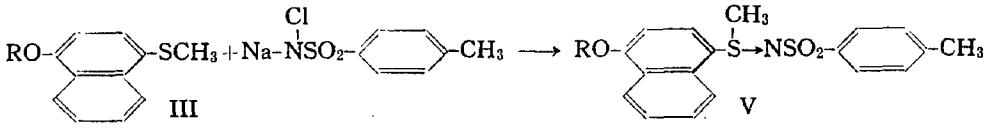
Table 1. REACTION OF 1-ALKOXY-4-THIOCYANATONAPHTHALENE WITH ALCOHOL IN THE PRESENCE OF SODIUM CYANIDE



Alkoxyl R	Alcohol R'	Reaction conditions		Products and Yields (%)	
		Temp (°C)	Time (h)	Sulfide (III)	Disulfide (IV)
CH_3	CH_3	reflux	6.5	94.4	trace
CH_3	CH_3	54~r. t.[b]	15.0	22.5	18.0
CH_3	C_2H_5	reflux	4.0	—	71.8
CH_3[a]	C_2H_5	24	4.5	—	74.0
CH_3	i-C_3H_7	reflux	8.5	—	50.0
C_2H_5	CH_3	reflux	1.5	50.0	44.3
C_2H_5[a]	CH_3	70	2.0	82.3	trace
C_2H_5	CH_3	31	4.0	50.0[c]	23.0
C_3H_7	CH_3	reflux	7.0	92.7	—
C_4H_9	CH_3	reflux	1.5	82.9	—
C_4H_9	CH_3	reflux	10.0	92.5	—
n-C_6H_{13}	CH_3	reflux	9.0	58.4	—
n-C_8H_{17}	CH_3	reflux	13.0	67.5	—
n-$C_{12}H_{25}$	CH_3	reflux	10.0	80.4	—

a) Two equivalents of NaCN were used.
b) Added at 54°C, then kept standing at room temperature.
c) The product is O-methyl S-4-ethoxynaphyl thioiminocarbonate (IIb).

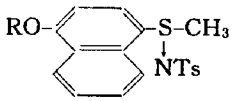
under reflux, and gave III in good yields (Table 1). As the compound for identification of III 4-alkoxynaphthyl methyl N-tosylsulfilimine (V) was prepared from III with chloramine T.[3]



Four characteristic intense bands[4] due to both sulfonyl and sulfilimino groups were observed in the infrared spectra of these new sulfilimines. The structures of III and V were established by IR, Mass, and NMR spectra and the elemental analyses (Table 2 and 3).

Formation of Disulfides and Thioiminocarbonate. In the reaction of 1-ethoxy-4-thiocyanatonaphthalene (Ib) with methanol at 31°C for 4 hr we found that a disulfide, bis (4-ethoxynaphthyl) disulfide (IVb),[2] was precipitated and a thioiminocarbonate, O-methyl S-ethoxynaphthyl thioiminocarbonate (IIb), was isolated from the filtrate.

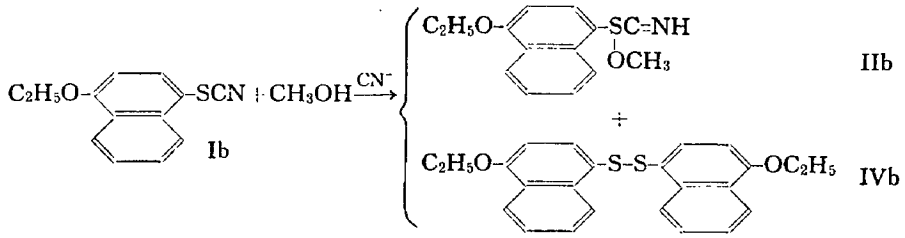
Table 2. PHYSICAL PROPERTIES OF 4-ALKOXYNAPHTHYL METHYL N-TOSYLSULFILIMINE



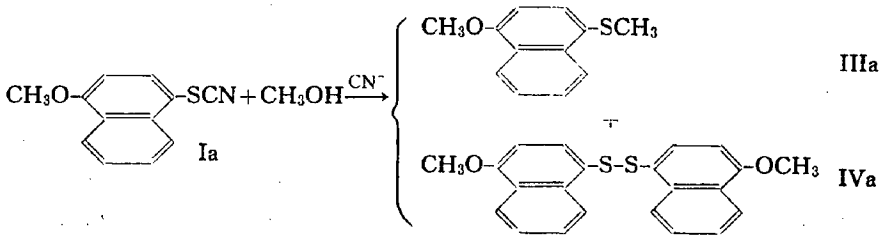
Compd No.	Alkoxyl R	Mp (°C)	Anal. %, Found (Calcd) C	H	N	NMR (δ) SCH_3	IR (cm^{-1}) $\nu_{-S\cdot\cdot N-}$	ν_s (SO_2)	ν as (SO_2)	
Va	CH_3	173	61.36(61.10)	4.98(5.13)	3.80(3.75)	2.87	928	1135	1271	1084
Vb	C_2H_5	167–168	62.33(61.99)	5.46(5.46)	3.62(3.61)	2.87	925	1145	1278	1090
Vc	C_3H_7	149–150	63.02(62.82)	5.76(5.77)	3.46(3.49)	2.87	952	1142	1270	1094
Vd	C_4H_9	152–154	63.85(63.59)	5.99(6.06)	3.34(3.37)	2.87	942	1142	1273	1088

Table 3. PHYSICAL PROPERTIES OF 4-ALKOXYNAPHTHYL METHYL SULFIDE AND THE RELATED COMPOUNDS

Compd No.	Alkoxyl R	Mp (°C)	Anal., %, Found (Calcd) C	H	S	MS (M^+)	NMR (δ) SCH_3	Vicinal proton of COR
IIIa	CH_3	64–66	70.63(70.55)	6.18(5.92)	15.83(15.70)	204	2.36(s)	6.55(d)
IIIb	C_2H_5	44	71.25(71.52)	6.53(6.46)	14.67(14.69)	218	2.37(s)	6.55(d)
IIIc	C_3H_7	40.2–40.5	72.49(72.37)	6.40(6.90)	13.87(13.80)	232	2.42(s)	6.67(d)
IIId	C_4H_9	29	73.26(73.13)	7.59(7.36)	12.91(13.01)	246	2.40(s)	6.65(d)
IIIe	n-C_6H_{13}	33–34	74.49(74.41)	8.05(8.08)	11.48(11.68)	272	2.45(s)	6.75(d)
IIIf	n-C_8H_{17}	39.5	75.27(75.45)	8.73(8.66)	10.33(10.60)	302	2.45(s)	6.76(d)
IIIg	n-$C_{12}H_{25}$	43.5	76.85(77.04)	9.53(9.56)	8.94(8.94)	358	2.48(s)	6.75(d)
IVa	CH_3	146	69.72(69.81)	4.82(4.79)	16.88(16.94)	378	—	6.46(d)
IIb	C_2H_5	86.5–88.5	64.51(64.34) N, 5.44(5.36)	5.86(5.79)	12.27(12.27)	261	—	6.71(d) 3.85(s, OCH_3) 6.6–7.0(br. NH)



Also, we found that the reaction of 1-methoxy-4-thiocyanatonaphthalene (Ia) with methanol at room temperature for 15 hr after the addition of NaCN at 54°C gave bis(4-methoxynaphthyl) disulfide (IVa) and 4-methoxynaphthyl methyl sulfide (IIIa).



The structures of IIb and IVa were confirmed by Mass and NMR spectra and elemental analyses (Table 3).

Mechanism of Reactions. On the basis of these results described above the process of formation of diaryl disulfide (IV) can reasonably be explained as following equations (2),[5] (3),[5] and (4).

$$\underset{\text{I}}{\text{ArSCN}} + \text{R'OH} \xrightarrow{CN^-} \underset{\text{II}}{\text{ArS-C(OR')=NH}} + CN^- \longrightarrow \text{ArS}^- + \text{R'OCN} + \text{HCN} \quad (2)$$

$$\text{ArS}^- + \text{R'OCN} \longrightarrow \underset{\text{III}}{\text{ArSR'}} + OCN^- \quad (3)$$

$$\text{ArS}^- + \underset{\text{I}}{\text{ArSCN}} \rightleftharpoons \underset{\text{IV}}{\text{ArS-SAr}} + CN^- \quad (4)$$

Alkoxynaphthalenethiolate anion, which is formed by the dissociation of II with the cyanide ion, is assumed to react with not only alkyl cyanate but also a further molecule of thiocyanate. The symmetrical diaryl disulfide thus formed is cleaved into aryl thiolate anion and the original thiocyanate on heating (from the right to left in Eq. 4) which then reacts with methanol used as the solvent to give III via the intermediate II. The former, aryl thiolate anion, reacts with alkyl cyanate to give III. Because the formation of IVa or IVb was always observed during the initial period of synthesis of the methyl sulfide (Eq. 1) and almost of IV disappeared at the end point of the reaction owing to the cleavage of IV induced by cyanide anion [6] Further addition of NaCN to the reaction mixture was therefore effective to afford IIIb in high yield as shown in Table 1. In order to confirm the scission of the sulfur-sulfur bond of IV by cyanide anion, IVb in methanol was treated with NaCN by heating under reflux for 1.5 hr to give IIIb in a moderate yield.

Further Survey of Reactions. In contrast with the reaction of I with methanol no ethyl or isopropyl sulfide was isolated but IVa in the reaction of Ia with ethanol or isopropyl alcohol at a low temperature or under reflux condition due to the affinity of ethyl or isopropyl cation for the thiolate anion is weaker than that of the methyl cation in Eq. 3.

Experimental

IR spectra were obtained in KBr disks on a Hitachi EPI G3 spectrophotometer and NMR spectra on a Japan Electron JNH-G-60 spectrometer in $CDCl_3$, using TMS as the internal standard.

Preparation of 4-Alkoxynaphthyl methyl sulfide (III) *from 1-Alkoxy-4-thiocyanatonaphthalene* (I). The thiocyanate (10 mmol) was dissolved in 60 ml of hot methanol. To this hot solution was added 0.5 g (10 mmol) of powdered NaCN. After the mixture had been refluxed gently on a steam bath for an appropriate period (see Table 1), the insoluble materials, such as sodium cyanate and bis(4-alkoxynaphthyl) disulfide, were removed by filtration, and then water was added to the filtrate until it became turbid. Colorless plates of III were obtained from the resulting solid after crystallization from alcohol-water.

Formation of O-Methyl S-4-ethoxynaphthyl thioiminocarbonate (IIb) *and Bis(4-ethoxynaphthyl) disulfide* (IVb) *in the Reaction of 1-Ethoxy-4-thiocyanatonaphthalene*

(Ib) *with Methanol in the Presence of Sodium Cyanide.* A solution of Ib (2.3 g; 10 mmol) and NaCN (0.5 g; 10 mmol) in methanol (95 ml) was stirred at 31°C for 4 hr. Resulting yellow precipitate (460 mg) was filtered, which was identified with an authentic sample of IVb[2] by mixed-melting point and IR spectrum. The filtrate became turbid on addition of 50 ml of cold water and after cooling for 3 hr 1.3 g of IIb was obtained as transparent plates after recrystallization from petroleum ether.

Formation of 4-Methoxynaphthyl methyl sulfide (IIIa) *and Bis(4-methoxynaphthyl) disulfide* (IVa) *in the Reaction of 1-Methoxy-4-thiocyanatonaphthalene* (Ia) *with Methanol in the Presence of Sodium Cyanide.* To a solution of 5.7 g (26 mmol) of Ia in methanol (200 ml) was added 1.4 g (26 mmol) of NaCN at 54°C. After the mixture had been stirred for 15 hr at room temperature, 0.9 g of IVa was precipitated as yellow plates. Then, most of the solvent was removed under reduced pressure at room temperature. The residue was filtered and 1.2 g of IIIa was isolated as white powder from the filtrate.

Formation of 4-Ethoxynaphthyl methyl sulfide (IIIb) *in the Reaction of Bis(4-ethoxynaphthyl) disulfide* (IVb) *with Cyanide Anion.* A solution of IVb (2.03 g; 5 mmol) and NaCN (0.5 g; 10 mmol in methanol (120 ml) was refluxed for 1.5 hr. By the preceding procedure IIIb was given in a 37% yield (800 mg) with small amount of unreacted disulfide.

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References

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5) These equations correspond to those of Tanaka *et al.*[1] who reported on a phenyl methyl sulfide.
6) K. Tanaka, J. Hayami, and A. Kaji, *Bull. Chem. Soc. Jpn.*, **45**, 536 (1972).